Condensation and evaporation

*Supersaturated* gases and *superheated* liquids owe their metastable existence to the surface tension \( \sigma \). Consider a liquid droplet in equilibrium with the surrounding vapor, implying \( T_l = T_g, \mu_l = \mu_g, \) and \( p_l > p_g \) because of surface tension.

For a vapor bubble surrounded by liquid, the argument proceeds along analogous lines.

Work done if droplet expands or contracts: \( \delta W = -p_l dV_l - p_g dV_g + \sigma dA \).

Grand potential: \( \Omega(T, V, \mu) = -p_l V_l - p_g V_g + \sigma A \).

\[
\Rightarrow \Omega(T, V, \mu) = -\frac{4\pi}{3} R^3 p_l - \left( V_{\text{tot}} - \frac{4\pi}{3} R^3 \right) p_g + 4\pi R^2 \sigma.
\]

Mechanical equilibrium: \( (\partial \Omega/\partial R)_{T,V,\mu} = 0 \Rightarrow 4\pi R^2 (p_g - p_l) + 8\pi R \sigma = 0. \)

Excess pressure in droplet: \( p_l - p_g = 2\sigma/R \).

Gibbs-Duhem equations (with \( dT = 0 \)), \( N_l d\mu_l = V_l dp_l, N_g d\mu_g = V_g dp_g \).

Chemical equilibrium: \( d\mu_l = d\mu_g \Rightarrow (V_l/N_l) dp_l = (V_g/N_g) dp_g \).

Differential excess pressure: \( d(p_l - p_g) = V_g/N_g - V_l/N_l \ dp_g = d \left( \frac{2\sigma}{R} \right) \).

Use \( V_g/N_g \gg V_l/N_l \), \( V_g/N_g \simeq \frac{k_B T}{p_g} \Rightarrow \frac{k_B T/p_g}{V_l/N_l} dp_g = d \left( \frac{2\sigma}{R} \right) \).

Integrate \( \frac{dp_g}{p_g} = \frac{V_l}{N_l k_B T} d \left( \frac{2\sigma}{R} \right) \) from \( \infty \) to \( R \).

\[
\Rightarrow \ln \frac{p_g(R)}{p_g(\infty)} = \frac{2\sigma V_l}{RN_l k_B T} = \frac{2\sigma m}{R \rho k_B T} \Rightarrow p_g(R) = p_g(\infty) \exp \left( \frac{2\sigma m}{R \rho k_B T} \right).
\]

Only liquid droplets of a particular radius \( R_c \) coexist with the supersaturated gas phase. Droplets with \( R < R_c \) will shrink. Droplets with \( R > R_c \) will grow. Hence the condensation process at pressure \( p = p_g(R_c) \) can be initiated by the presence of droplets with radius \( R > R_c \).

Metastability depends on the absence of droplets with radius \( R > R_c \). The boundary of the metastable region (spinodal line) corresponds to a value of \( R_c \) comparable to the molecular radius. Supersaturation cannot be pushed beyond that point.